

CXC.—*The Relation between Absorption Spectra and Chemical Constitution. Part XI. Some Aromatic Hydrocarbons.*

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IN an investigation on the absorption spectra of a number of derivatives of naphthalene, undertaken with the view of determining the influence of substitution, we have made a careful study of the absorption spectrum of naphthalene. Realising the great importance of this spectrum, we have taken every precaution as regards the purity of the naphthalene, and have used more than one source of light in order to guard against any error arising from inequalities in the spectrum of the source.

The purest naphthalene was obtained from Kahlbaum, and this was heated with manganese dioxide and concentrated sulphuric acid, after which it was distilled in a current of steam. This process was repeated, and then the naphthalene was converted into the picrate, this compound being carefully recrystallised. The naphthalene, after regeneration, was again distilled in a current of steam, and then recrystallised from dilute alcohol. The absorption curve we obtained with the pure compound is shown in Fig. 1 (full curve); there are three absorption bands, namely, two narrow ones at $1/\lambda = 3125$ and 3220 respectively, and a third broad band with its head at about $1/\lambda = 3700$. Our curve differs from that given by Hartley (Trans., 1885, **47**, 685) in not showing bands at $1/\lambda = 3270$ and 3370 .

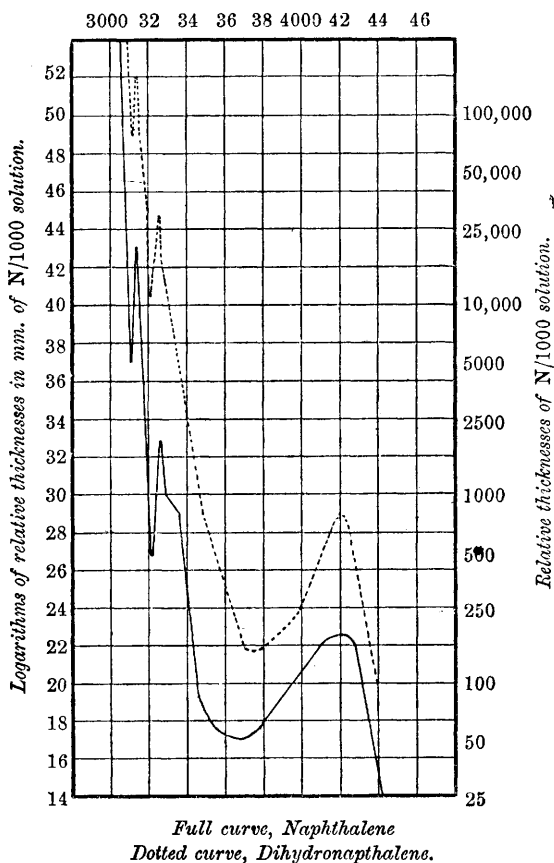
The absorption of naphthalene is of peculiar interest, since, owing to the structure of the compound, two ethylenic linkings are conjugated with a benzene nucleus, the whole forming one closed system. Among the substituted aromatic compounds which have been dealt with up to the present, there have only been included those in which the unsaturated centres are attached to the benzene nucleus at one point. It would appear from previous observations that the absorption spectrum of a benzene compound containing a side-chain with ethylenic double linkings shows one broad absorption band. A good example of this is stilbene, the absorption curve of which is shown in Fig. 4 (dotted curve). We are therefore able to say that when we have centres of residual affinity, as expressed by ethylenic linkings attached at one point to a benzene ring, the resulting isorropesis gives rise to a single absorption band which is much nearer to the red than the bands

of benzene, the amount of the shift being dependent upon the number of ethylene linkings in the side-chain.

The case is different, however, when the unsaturated system is attached at two points to the benzene ring; the absorption is of a very different type, as can be seen from the curves of

FIG. 1.

Oscillation frequencies.

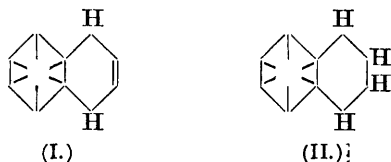


naphthalene, anthracene, and phenanthrene. In these cases, and in all the hydrocarbons examined of this type, there is always present in the absorption a band very close to the position of the benzene bands, and also small bands or groups of bands appearing nearer the red end of the spectrum and at greater concentra-

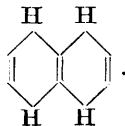
tion. In these cases, therefore, we have direct evidence that true benzenoid motions are taking place, and that also there are new free periods of vibration due to the isorropesis between the ethylenic linkings and the benzene ring. This type of oscillations is due in some way to the fact that the unsaturated side-chain is doubly linked to the phenyl group, for if there be only a single point of attachment the system acts as a whole, giving only one free period of vibration.

In reference to this linking together of the systems, it is interesting to compare the absorption of hexatriene, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, with that of benzene. The absorption of the former is shown in Fig. 4 (dot and dash curve), and, as can be seen, only shows general absorption, whereas in benzene, which contains the same number of ethylenic linkings, we have a complicated system of absorption bands due to the play of forces which become possible owing to the formation of the ring.

It is necessary, in forming any views on the play of forces in naphthalene, to consider the chemical behaviour of the compound. From the ease with which naphthalene is reduced in hot alcoholic solution by metallic sodium to the dihydro-compound (I),



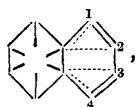
and the further reduction to the tetrahydro-compound (II) by the action of sodium on a hot solution in amyl alcohol, this being the final product of reduction (Bamberger and Lodter, *Ber.*, 1887, **20**, 3075; Bamberger and Kitchelt, *Ber.*, 1890, **23**, 1561), there is little doubt that one of the rings is truly benzenoid, and the other contains two ethylenic double bonds which, according to Thiele's law, give their maximum effect at the two extremes; that is to say, at the positions 1 and 4. Again, reduction of both rings takes place only when naphthalene is heated with phosphorus and hydriodic acid, a method which will reduce benzene itself. It is interesting to note that one of the first compounds produced by the action of phosphorus and hydriodic acid on naphthalene is the α -tetrahydro-compound,



This reduction no doubt takes place in two stages: first, the addition of an atom of hydrogen at the two extremes of the conjugated ethylenic double linkings, as in the case of the action of metallic sodium on a solution of naphthalene in alcohol; secondly, the addition of hydrogen to the top and bottom of the benzenoid ring, a reduction which would follow naturally from the motions of the benzene ring as put forward in a previous paper (Baly, Edwards, and Stewart, *Trans.*, 1906, **89**, 514), where it was shown that the maximum unsaturation occurs in benzene at two carbon atoms opposite to one another.

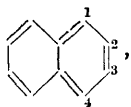
Naphthalene therefore would seem to consist of two rings, of which one is truly benzenoid, and the other contains two conjugated double linkings. There is no reason to insist that there is no possibility of an interchange of the characteristics from one ring to the other, that is, there is no reason to insist that the two rings are permanently endowed with one of the two above characters; in fact, it seems that the interchange of these characters between the rings is perfectly possible, and no doubt is continually taking place.

In seeking the origin of the three absorption bands in the spectrum of naphthalene, it may be said at once that the broad absorption band with its head at $1/\lambda = 3700$ is due to the benzenoid motions of the naphthalene molecule; we may attribute this band therefore to the half of the molecule which is benzenoid in character. The two narrow bands of $1/\lambda = 3125$ and 3220 , which are much nearer to the red than any of the benzene bands, must be due to the isorropesis between the benzenoid tautomerism of the ring and the ethylenic double linkings of the other. If the molecule of naphthalene is written



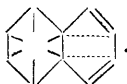
with the centric formula to represent the benzenoid ring, it is evident that the interference or isorropesis between the ethylene system and the benzenoid system can be imagined to occur either between the atoms 1, 4, and the benzenoid ring, or between the atoms 2, 3, and the benzenoid ring. In the figure this possible play of forces is denoted by the two pairs of dotted lines. Now the first alternative, namely, the isorropesis between the atoms 1, 4, and the benzenoid system, does not seem to be valid, because it is merely the first stage in the interchange of character between the two rings. If the dotted lines between the atoms 1, 4, and the

adjacent ring represent real double linkings, the molecule would become



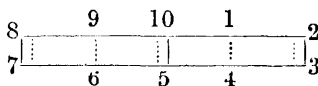
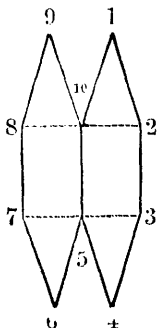
or, in other words, the ring 1:2:3:4 would now be the benzenoid ring, whilst the other would contain the ethylenic system. Inasmuch as it is necessary to have isorropesis or interference between two separate and distinct systems in order to produce bands of smaller free period than the benzene bands, so it would not seem possible to attribute either of the naphthalene bands at $1/\lambda = 3125$ and 3220 to the above process, a process which is merely a step in the interchange of character between the two naphthalene rings.

We are thus left with the second alternative, namely; the isorropesis between the atoms 2 and 3, with the benzenoid system as expressed by the dotted lines:



This is the only way in which the two systems, ethylenic and benzenoid, can give an interference system without either of them losing their character.

This may be made clearer by the conception that the naphthalene molecule is in a state of pulsation in somewhat the same way as has already been suggested for the benzene molecule (Baly, Edwards, and Stewart, *loc. cit.*):



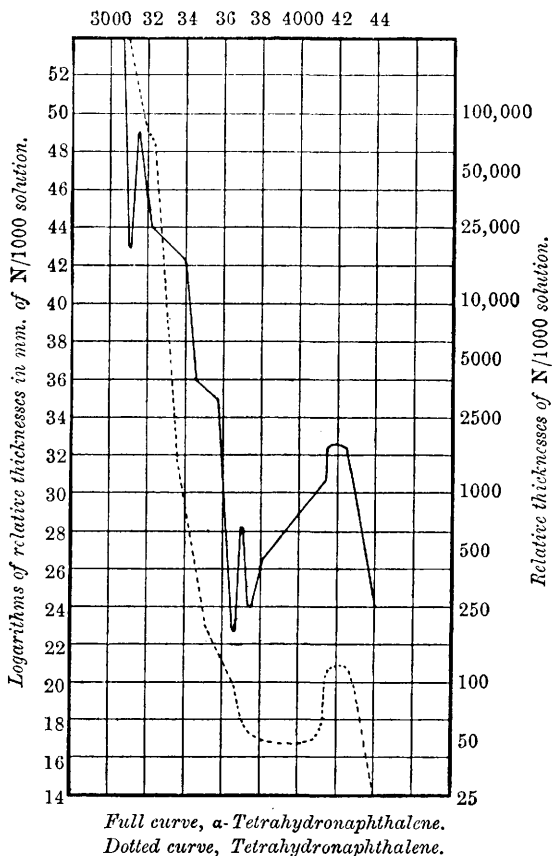
The molecule would then have two extreme phases, as shown in the figures, and the readiness with which isorropesis can arise

between the ethylenic and benzenoid systems through the atoms 2 and 3 is at once apparent.

It is evident that the two central atoms 5 and 10 are the two most important to be considered in determining the types of isorropesis arising in the naphthalene molecule. In a previous

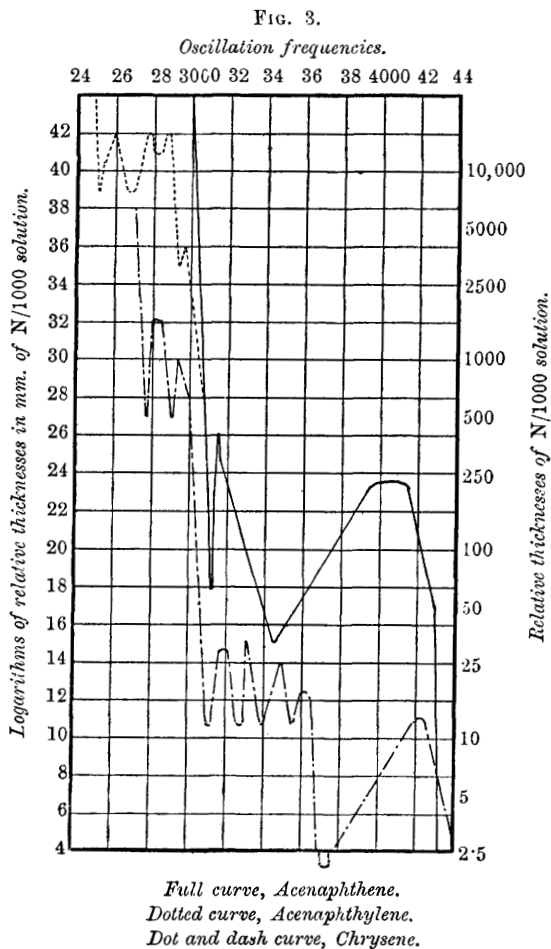
FIG. 2.

Oscillation frequencies.



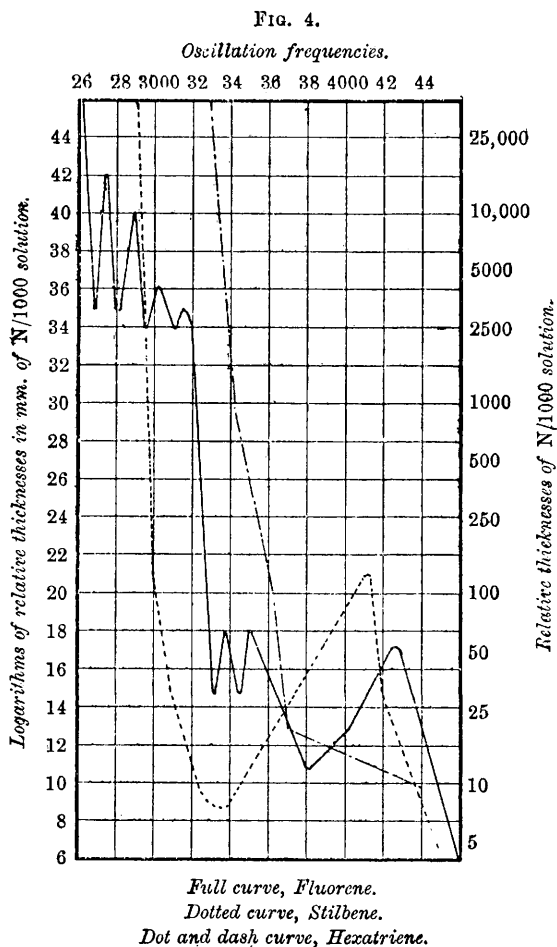
paper (Baly and Collie, Trans., 1905, **87**, 1332) on the dynamics of the benzene molecule, it was shown that each carbon atom is concerned in the making and breaking of an ortho-, meta-, and para-linking respectively. In naphthalene, however, the two carbon atoms 5 and 10 can only be concerned in making and breaking of an ortho- and meta-linking respectively, for unless the rings are

distorted to an inconceivable degree, the atoms 5 and 8 cannot approach one another sufficiently near to enable a para-linking to be formed, the same being true of the atoms 10 and 7. As far as the isorropesis is concerned, only two types are possible, namely, (1) when the atoms 5 and 10 are making and breaking

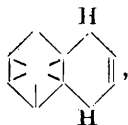


an ortho-linking; and (2) when the atoms 5 and 10 are making and breaking a meta-linking. There should, according to this view, be only two isorropesis bands in the absorption spectrum of naphthalene, and, indeed, we find only two, namely, those at $1/\lambda = 3125$ and 3220 . It is possible to put this explanation to a somewhat rigid test by examining the absorption spectra of dihydro-

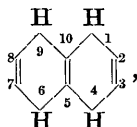
naphthalene and the two tetrahydro-compounds. If our theory is correct, it is a simple matter to forecast the absorption spectra of these compounds. Thus the tetrahydronaphthalene with one ring entirely reduced should merely show absorption due to



benzenoid tautomerism of the remaining ring, without either of the isorropesis bands. The dihydronaphthalene,

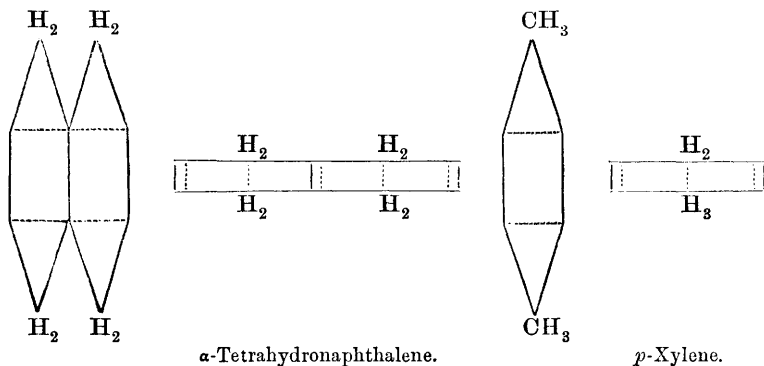


should exhibit an absorption very similar to that of naphthalene, since the residual affinity of the atoms 2 and 3 is only slightly reduced, so that the play of forces within the molecule is only slightly lessened in degree. The so-called α -tetrahydronaphthalene,



is peculiarly interesting, because the play of forces is rendered very much simpler. One possibility, namely, the make and break of linking between the ortho-atoms 5 and 6 and 10 and 9, has been entirely eliminated, so that we should expect one of the isorropesis bands to be removed. These three compounds have been prepared and their spectra examined, and, as can be seen on reference to Fig. 1 (dotted curve) and Fig. 2 (both curves), they conform absolutely to what the theory foretold.

A further point of interest arises in connexion with α -tetrahydronaphthalene; both rings are now exactly similar, and so the pulsating movements of the molecule should be more regular and less distorted than in naphthalene itself. In fact, the motions may be directly compared with those of *p*-xylene, and may be represented in their extreme phases as follows:

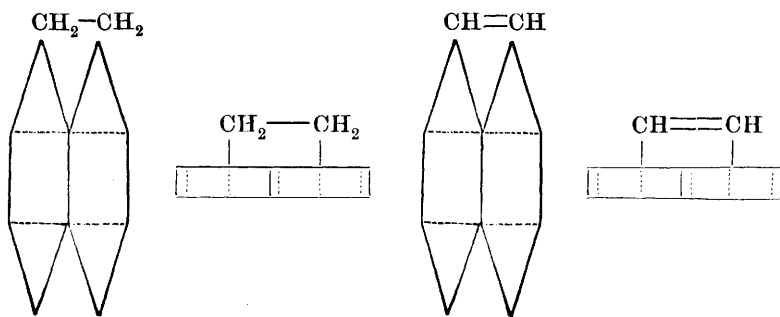


The benzenoid absorption bands of α -tetrahydronaphthalene should closely resemble those of *p*-xylene. The absorption of *p*-xylene has already been described (Baly and Ewbank, Trans., 1905, 87, 1355), and shows two absorption bands of exactly the same type and in exactly the same position as the two of α -tetrahydronaphthalene. The oscillation frequencies of the heads of the bands in each case are:

$$1/\lambda = 3650 \text{ and } 3730.$$

The three reduced naphthalenes thus afford complete support to the theory advanced above, and, moreover, enable us to determine which of the two isorropesis bands of naphthalene can be attributed to each of the two isorropic processes. The results obtained with the α -tetrahydro-compound show that the band at $1/\lambda = 3125$ is due to the isorropesis when the carbon atoms 5 and 10 are undergoing a make and break of a meta-linking, so that the band at $1/\lambda = 3220$ is due to the isorropesis occurring when the atoms 5 and 10 are undergoing a make and break of an ortho-linking.

We have been encouraged by these results to examine the absorption of some other aromatic hydrocarbons, namely, acenaphthene, acenaphthylene, fluorene, anthracene, chrysene, phenanthrene, dibenzyl, and diphenyl. The absorption curves of the first two are shown in Fig. 3 (full and dotted curves), and, as can be seen, are identical for the smaller concentrations, whilst at higher concentrations acenaphthylene shows a new set of bands (to which its visible colour is due). These last-mentioned bands must clearly be due to the isorropesis arising from the external double linking. A very striking similarity between both these compounds and naphthalene is to be seen, for they exhibit very strongly the band at $1/\lambda = 3123$. This is the band which appears in α -tetrahydronaphthalene, so that the pulsating motions of acenaphthene and acenaphthylene must be very similar to those of naphthalene. This, however, is only to be expected from their structure, since we must have the two extreme phases respectively:



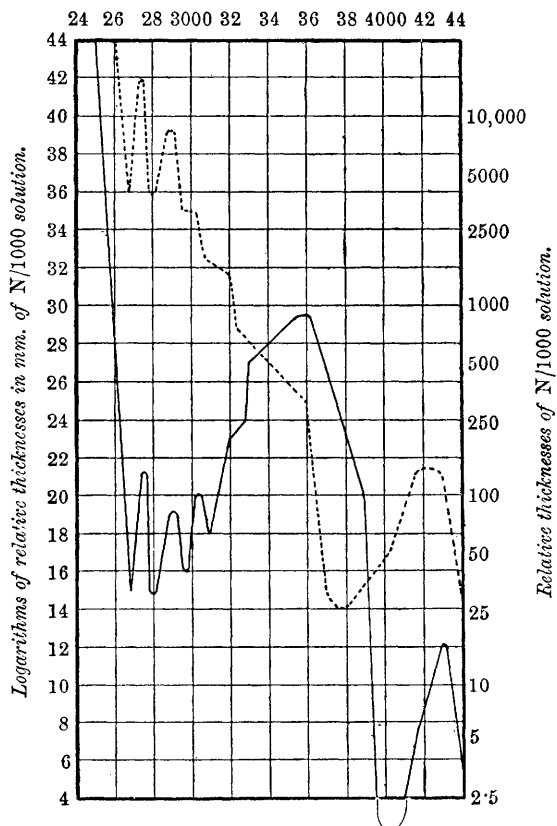
The curves of fluorene and anthracene are shown in Figs. 4 and 5 (full curves), and, as can be seen, show a marked similarity in that they both possess the four isorropesis bands at $1/\lambda = 2680, 2800, 2980$, and 3090 , although the shape of the curves are materially different in other respects. In Fig. 5 (dotted curve) is shown the

absorption curve of dihydroanthracene, which only differs from fluorene by the additional CH_2 group:



FIG. 5.

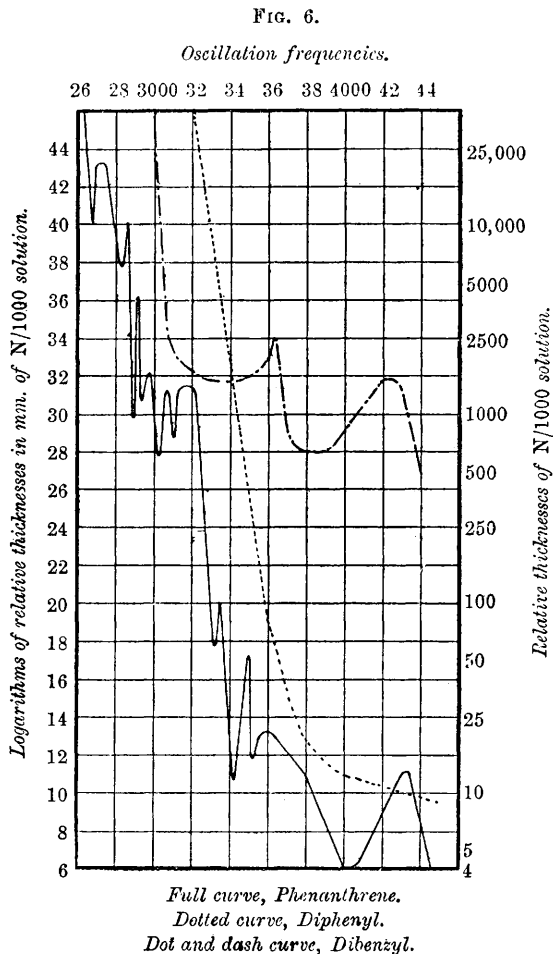
Oscillation frequencies.



*Full curve, Anthracene.
Dotted curve, Dihydroanthracene.*

The curves of the two are very similar, but two of the isorropesis bands of fluorene are almost absent in the curve of dihydroanthracene. The play of forces occurring in the three last compounds is dependent on the CH_2 group, which possesses a peculiar type of residual affinity which we propose to submit to future

investigation. This residual affinity depends on the substitution of the hydrogen atoms of methane by electro-negative groups, and evidences of this have already been observed in the case of benzyl alcohol and benzyl ethyl ether (Baly and Collie, *loc. cit.*), which both show small bands due to isorropesis between the phenyl group



and the side-chain. This effect is most strikingly exhibited in dibenzyl, the absorption curve of which is shown in Fig. 6 (dot and dash curve).

The absorption curves of chrysene and phenanthrene are shown in Fig. 3 (dot and dash curve) and Fig. 6 (full curve), and, although

certain regularities can be observed, the motions are too complex to permit of their elucidation until after the reduced derivatives have been examined.

In order to complete the series, we have included the absorption curve of diphenyl (Fig. 6, dotted curve), which only shows general absorption.

The absorption spectra of phenanthrene and anthracene have also been examined by Hartley (Trans., 1881, **39**, 153), and only minor differences are to be noted in our curves.

Conclusions.

1. The absorption spectrum of naphthalene shows three absorption bands, two narrow ones at $1/\lambda = 3125$ and 3220 , and a broad one at about $1/\lambda = 3700$. The third of these is due to the benzenoid motions of one ring, whilst the first two are due to the isorropesis between the benzenoid motions of one ring and the ethylenic system of double linkings of the other.

2. The isorropesis can be explained by adopting the view that the naphthalene molecule is in a state of pulsation like the benzene molecule. Evidence of this pulsation is especially strong in the cases of α -tetrahydronaphthalene, acenaphthene, and acenaphthylene.

3. The absorption spectra show that very similar play of forces are present in fluorene, anthracene, and dihydroanthracene. These are due to the presence of the CH_2 group, the inherent character of which is at present being studied.

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